

Catalyst system comprising magnesium halide

The present invention relates to a catalyst system comprising a single site catalyst component containing a transition metal, supported on an adduct containing magnesium halide, and an organoaluminum compound.

Single site catalyst components are well known in the art and are usually used in conjunction with alumoxanes or boron compounds as cocatalysts in polymerization processes. The catalyst systems so obtained can be used supported on an inert support in order to control the morphology of the obtained polymer and to avoid fouling in the reactor, especially in a gas-phase or slurry polymerization processes.

The drawback of the catalyst systems so obtained is that since alumoxanes need to be used in large excess with respect to the single site catalyst components, the resulting catalyst is very expensive. Therefore it is desirable to reduce or eliminate the use of alumoxanes.

When boron compounds are used as cocatalyst, a large excess is not required. However they have the drawback of being more expensive than alumoxanes and dangerous to handle.

Magnesium chloride is a well-known support for classic Ziegler Natta catalyst systems based on TiCl_4 or TiCl_3 . The use of this compound as a carrier for single-site catalysts could be very advantageous, in view of its chemical and structural simplicity, and the possibility to finely control the porosity of this support and, therefore, to easily tune the porosity of the final catalyst system.

Adducts containing magnesium chloride and an organoaluminum compound have already been proposed as supports for metallocene-based catalyst components in which the central atom is zirconium, titanium or hafnium. For example, in *Macromol. Chem. Phys.* 195, 1369-1379 (1984), MgCl_2 in combination with a zirconocene catalyst and trialkylaluminum is used. More recently, In *Macromolecules* 1993, 26, 4712, mixtures of MgR_2 and AlR_2Cl (generating MgCl_2 and AlR_3) as cocatalyst components for olefin polymerization using various metallocenes have been used. In various papers, namely, *Korean J. Chem. Eng.* 16(5) 562-570, *Journal of Applied Polymer science* Vol 70, 1707-1715, *Korean J. Chem. Eng.* 19(4) 557-563 and *J. Molec. Catal A* 191, 2003, 155-165, Lee and co-workers proposed a metallocene-based catalyst system in which alcohol and anhydrous MgCl_2 are reacted to form an adduct MgCl_2 -alcohol. The adduct, further reacted

with trialkylaluminum, is used for supporting zirconocene compounds. The obtained catalyst system can be used without a further addition of alumoxanes.

However, there is still the need to find alternative, easily obtainable supports for other kinds of single site catalyst system allowing elimination of the use of alumoxanes or boron compounds.

An object of the present invention is therefore a supported catalyst system comprising the product obtainable by contacting:

- a) an adduct of formula (I)



wherein

Mg is magnesium; Al is aluminum; O is oxygen;

T is chlorine, bromine, or iodine, preferably chlorine;

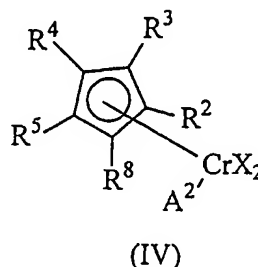
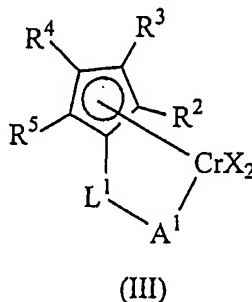
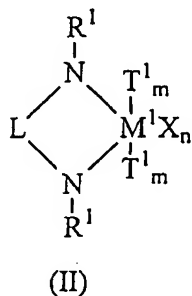
U is a linear or branched C₁-C₁₀ alkyl radical, preferably U is a linear C₁-C₁₀ alkyl radical; more preferably U is a methyl or an ethyl radical;

y ranges from 6.00 to 0.05; preferably y ranges from 2 to 0.1, more preferably from 1 to 0.1;

j ranges from 3 to 0.1, preferably from 3 to 0.5; more preferably from 3 to 1 being also a non integer number;

Q substituent, same or different, is a hydrocarbon radical containing from 1 to 20 carbon atoms optionally containing silicon or germanium atoms; preferably Q is a linear or branched, cyclic or acyclic, C₁-C₂₀-alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl or C₇-C₂₀-arylalkyl radicals optionally containing silicon or germanium atoms; more preferably Q is a linear or branched C₁-C₂₀-alkyl radical; even more preferably Q is an ethyl, a n-propyl, an iso-propyl, a n-butyl, an iso-butyl, a tert-butyl, a hexyl or an octyl radical;

- b) with at least one compound selected from the compounds of formula (II), (III) and (IV)



wherein:

in the compound of formula (II):

M^1 is a transition metal atom selected from Groups 3-11 of Periodical Table (Group 3 including lanthanoids); preferably M^1 is a transition metal atom selected from Groups 3-6 and 8-10, more preferably M^1 is a transition metal atom selected from Groups 4, 5, and 6; still more preferably M^1 is a metal of Group 4 or 5: specifically including scandium, titanium, zirconium, hafnium, vanadium, niobium, tantalum, cobalt, rhodium, yttrium, chromium, molybdenum, tungsten, manganese, rhenium, iron, ruthenium, nickel, and palladium; preferably scandium, titanium, zirconium, hafnium, vanadium, niobium, tantalum, iron, cobalt, rhodium, nickel, and palladium; more preferably titanium, zirconium, hafnium, vanadium, nickel, niobium, tantalum, chromium, and molybdenum; still more preferably titanium, vanadium and nickel;

the substituents X, equal to or different from each other, are monoanionic sigma ligands selected from the group consisting of hydrogen, halogen, R, OR, OCOR, SR, NR_2 and PR_2 , wherein R is a hydrocarbon radical containing from 1 to 20 carbon atoms, optionally containing one or more Si or Ge atoms; preferably X is an halogen atom or a R group; more preferably X is chlorine or a C_1 - C_{10} alkyl radical, such as a methyl or an ethyl radical;

n ranges from 0 to 3; preferably n is 2;

the bonds connecting the two nitrogen atoms with the bridge L can be single bonds or double bonds;

L is a divalent or trivalent bridge connecting the two nitrogen atoms; preferably L is a divalent or trivalent C_1 - C_{40} hydrocarbon group, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements;

each R^1 , equal to or different from each other, is a C_1 - C_{40} hydrocarbon radical optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; preferably R^1 is a hydrogen atom, or a linear or branched, cyclic or acyclic, C_1 - C_{20} -alkyl, C_2 - C_{20} alkenyl, C_2 - C_{20} alkynyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl or C_7 - C_{20} -arylalkyl radical optionally containing silicon atoms;

m ranges from 0 to 1; when m is 0 the group T^1 is not-existent;

T^1 is a Lewis base, such as tetrahydrofuran, tertiary amine, pyridine, pyrrole and the like. The group T^1 can also be bonded to the group R^1 ;

in the compound of formula (III):

Cr is a chromium atom; X is as described above;

each R^2 , R^3 , R^4 and R^5 , equal to or different from each other, is a hydrogen atom, a halogen atom, or a C_1 - C_{40} hydrocarbon radical optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; or two adjacent R^2 , R^3 , R^4 and R^5 form one or more C_3 - C_7 membered ring optionally containing heteroatoms belonging to groups 13-17 of the periodic table; preferably each R^2 , R^3 , R^4 and R^5 , equal to or different from each other, is a hydrogen atom, halogen atom or a linear or branched, cyclic or acyclic, C_1 - C_{20} -alkyl, C_2 - C_{20} alkenyl, C_2 - C_{20} alkynyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl or C_7 - C_{20} -arylalkyl radical; or two adjacent R^2 , R^3 , R^4 and R^5 can form one or more C_3 - C_7 membered ring;

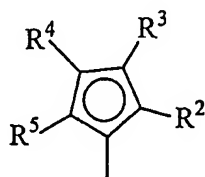
L^1 is a divalent bridging group selected from a C_1 - C_{20} alkylidene, a C_3 - C_{20} cycloalkylidene, a C_6 - C_{20} arylidene, a C_7 - C_{20} alkylarylidene, or a C_7 - C_{20} arylalkylidene radical optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements, and a silylidene radical containing up to 5 silicon atoms such as $SiMe_2$, $SiPh_2$; preferably L^1 is a divalent group $(ZR^6_{m1})_{n1}$; Z being C, Si, Ge, N or P, and each R^6 group, equal to or different from each other, is a hydrogen atom or a hydrocarbon group containing from 1 to 20 carbon atoms, or two R^6 can form an aliphatic or aromatic C_4 - C_7 ring; preferably R^6 is a hydrogen atom or a linear or branched, cyclic or acyclic, C_1 - C_{20} -alkyl, C_2 - C_{20} alkenyl, C_2 - C_{20} alkynyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl or C_7 - C_{20} -arylalkyl radical;

more preferably L^1 is selected from $Si(CH_3)_2$, $SiPh_2$, $SiPhMe$, $SiMe(SiMe_3)$, CH_2 , $(CH_2)_2$, $(CH_2)_3$ or $C(CH_3)_2$;

$m1$ is 1 or 2, and more specifically $m1$ is 1 when Z is N or P, and $m1$ is 2 when Z is C, Si or Ge;

$n1$ is an integer ranging from 1 to 4; preferably $n1$ is 1 or 2;

A^1 is a moiety of formula (V)



(V)

wherein R^2 , R^3 , R^4 and R^5 are as described above; or A^1 is an oxygen atom, a sulphur atom, a NR^7 , NR^7_2 , a OR^7 or a SR^7 group, wherein R^7 , is a C_1 - C_{40}

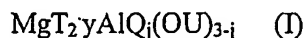
hydrocarbon radical, preferably R^7 is a linear or branched, cyclic or acyclic, C_1 - C_{20} -alkyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl or C_7 - C_{20} -arylalkyl radical; more preferably R^7 is a C_1 - C_{20} -alkyl radical, such as a methyl or an ethyl radical; preferably A^1 is a NR^7_2 group;

in the compound of formula (IV):

Cr is chromium; X , R^2 , R^3 , R^4 and R^5 are as described above, and R^8 has the same meaning given for R^2 , R^3 , R^4 and R^5 ;

A^2 is halogen, R^7 , OR^7 , $OCOR^7$, SR^7 , NR^7_2 , NR^7_3 , SR^7_2 , OR^7_2 wherein R^7 is as described above; preferably A^2 is a NR^7_3 group.

The adduct of formula (I)



generally has a surface area (BET) higher than $30 \text{ m}^2/\text{g}$; more preferably higher than $38 \text{ m}^2/\text{g}$; even more preferably higher than $200 \text{ m}^2/\text{g}$; but it can reach values higher than $300 \text{ m}^2/\text{g}$. It can be obtained with methods commonly known in the art. For example the adduct MgT_2wUOH , wherein w ranges from 0.1 to 6, is contacted with an aluminum compound of formula $H_eAlQ^{1}_{3-e}$ or $H_eAl_2Q^{1}_{6-e}$, in an inert solvent; where each Q^1 substituent, same or different, is hydrogen atom, halogen atom, or a hydrocarbon radical containing from 1 to 20 carbon atoms optionally containing silicon or germanium atoms; with the proviso that at least one Q^1 is different from halogen, and e ranges from 0 to 1, being also a non-integer number; preferably said hydrocarbon radicals is a linear or branched, cyclic or acyclic, C_1 - C_{20} -alkyl, C_2 - C_{20} alkenyl, C_2 - C_{20} alkynyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl or C_7 - C_{20} -arylalkyl radical optionally containing silicon or germanium atoms; preferably Q^1 is a linear or branched C_1 - C_{20} -alkyl radical; more preferably Q^1 is an ethyl, a n-propyl, an iso-propyl, a n-butyl, an iso-butyl, a tert-butyl, a hexyl or an octyl radical. Examples of this reaction can be found in US 4,399,054 and US 5,698,487.

Preferably the adduct of formula MgT_2wUOH is partially dealcoholated as described in US 5,698,487. Therefore a further object of the present invention is a supported catalyst system obtainable by the process comprising the following steps:

- a) contacting
 - (i) a partially dealcoholated adduct of formula MgT_2wUOH wherein T is chlorine, bromine, or iodine, preferably chlorine; U is a linear or branched C_1 - C_{10} alkyl radical, preferably U is a linear C_1 - C_{10} alkyl radical; more preferably

U is a methyl or an ethyl radical; w ranges from 6 to 0.1, preferably from 3 to 0.5; more preferably from 2.9 to 0.5 being also a non integer number; with

- (ii) an organo-aluminium compound of formula $H_eAlQ^1_{3-e}$ or $H_eAl_2Q^1_{6-e}$, wherein each Q^1 substituent, same or different, is a hydrogen atom, a halogen atom, or a hydrocarbon radical containing from 1 to 20 carbon atoms optionally containing silicon or germanium atoms; with the proviso that at least one Q^1 is different from halogen, and e ranges from 0 to 1, being also a non-integer number; preferably said hydrocarbon radical is a linear or branched, cyclic or acyclic, C_1 - C_{20} -alkyl, C_2 - C_{20} alkenyl, C_2 - C_{20} alkynyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl or C_7 - C_{20} -arylalkyl radical optionally containing silicon or germanium atoms; preferably Q^1 is a linear or branched C_1 - C_{20} -alkyl radical; more preferably Q^1 is an ethyl, a n-propyl, an iso-propyl, a n-butyl, an iso-butyl, a tert-butyl, a hexyl or an octyl radical;

to obtain an adduct of formula (I) $MgT_2yAlQ_j(OU)_{3-j}$ described above; and

- b) contacting the product obtained from step a) with at least one compound selected from the compounds of formula (II), (III) and (IV) as described above.

The partially dealcoholated adduct of formula MgT_2wUOH used in step a) can be obtained by partial dealcoholation of adducts of MgT_2 with alcohols, said adducts contains from 1 to 6 mol of alcohol. It is possible that two adducts having the same content of alcohol, i.e. having the same empirical formula, are different in porosity and surface area for the reason that one adduct is partially dealcoholated.

The dealcoholation can be carried out according to known methodologies such as those described in US 5,698,487. Depending on the extent of the dealcoholation treatment, partially dealcoholated adducts can be obtained having an alcohol content generally ranging from 0.1 to 3 moles of alcohol per mole of MgT_2 , preferably from 2.9 to 0.5; more preferably from 2.9 to 1.

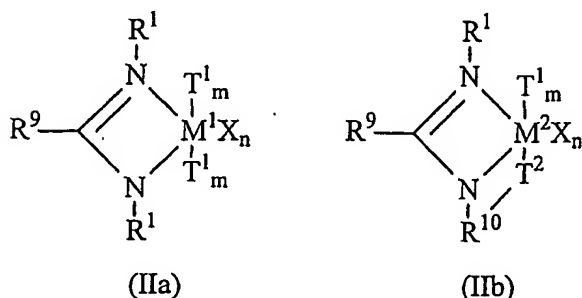
Said partially dealcoholated magnesium adduct is then contacted with an organo-aluminium compound of formula $H_eAlQ^1_{3-e}$ or $H_eAl_2Q^1_{6-e}$ in an inert solvent with methods common known in the art, such as the method described in EP-A-553 806.

In step b) of the process of the present invention at least one compound of formula (II), (III), and (IV) can be supported on the carrier obtained in step a) according to known methods by bringing the product of step a) into contact, for example, with a solution of the said compound, operating at temperatures between room temperature and 120°C. The

amount of said compound that is not fixed on the support is removed by filtration or similar methods.

The amount of said compounds supported on the adduct of formula (I) is generally between 1000 $\mu\text{mol/g}$ of support and 1 $\mu\text{mol/g}$ of support; preferably said amount ranges from 500 $\mu\text{mol/g}$ of support to 2 $\mu\text{mol/g}$ of support; more preferably from 200 $\mu\text{mol/g}$ of support to 2 $\mu\text{mol/g}$ of support.

Preferably, the compound of formula (II) has formulas (IIa) or (IIb)



wherein R^1 , T^1 , M^1 , X , m and n are as described above;

R^9 is a hydrogen atom or a linear or branched, cyclic or acyclic, C_1 - C_{20} -alkyl, C_2 - C_{20} alkenyl, C_2 - C_{20} alkynyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl or C_7 - C_{20} -arylalkyl radical optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of Elements; preferably R^9 is a C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl or C_7 - C_{20} -arylalkyl radical;

R^{10} is a divalent group selected from C_1 - C_{20} alkylidene, C_3 - C_{20} cycloalkylidene, C_6 - C_{20} arylidene, C_7 - C_{20} alkylarylidene, or C_7 - C_{20} arylalkylidene radical optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements, and a silylidene radical containing up to 5 silicon atoms; preferably R^{10} is a C_1 - C_{20} alkylidene radical; more preferably it is an ethylidene or a propylidene radical;

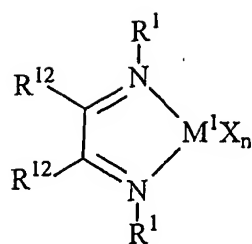
T^2 is an OR^{11} , SR^{11} or a NR^{11}_2 radical, wherein R^{11} is a linear or branched, cyclic or acyclic, C_1 - C_{10} -alkyl, C_2 - C_{10} alkenyl, C_2 - C_{10} alkynyl, C_6 - C_{10} -aryl, C_7 - C_{10} -alkylaryl or C_7 - C_{10} -arylalkyl radical;

preferably T^1 is tetrahydrofuran, a tertiary amine, pyridine or pyrrole;

preferably M^1 is titanium or vanadium;

preferably n is 2 and preferably m is 1;

in a further embodiment, the compound of formula (II) has formula (IIc),



(IIc)

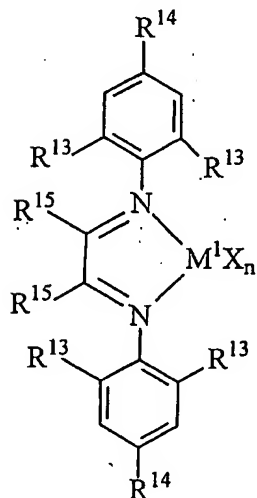
wherein R^1 , T^1 , M^1 , X , and n are as described above;

each R^{12} , equal to or different from each other, is a hydrogen atom or a linear or branched, cyclic or acyclic, C_1 - C_{20} -alkyl, C_2 - C_{20} alkenyl, C_2 - C_{20} alkynyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl or C_7 - C_{20} -arylalkyl radical optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; two R^{12} groups can also join to form a C_3 - C_8 membered ring that can bear one or more C_1 - C_{15} -alkyl, C_2 - C_{15} alkenyl, C_2 - C_{15} alkynyl, C_6 - C_{15} -aryl, C_7 - C_{15} -alkylaryl or C_7 - C_{15} -arylalkyl substituents;

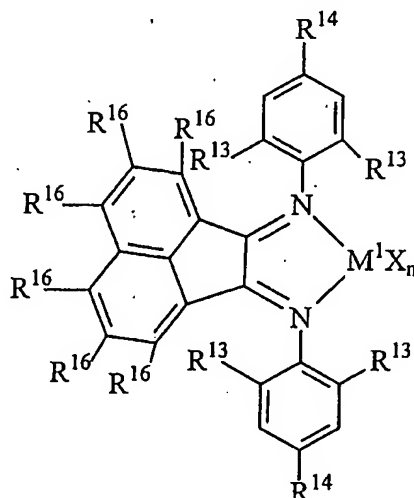
preferably R^1 is a C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl or C_7 - C_{20} -arylalkyl radical;

preferably M^1 is nickel and n is 2; X is preferably bromine.

Preferred compounds belonging to formula (IIc) are compounds of formula (IIca) and (IIcb)



(IIIca)



(IIIcb)

wherein:

each R^{13} , equal to or different from each other, is a hydrogen atom or a linear or branched, cyclic or acyclic, C_1 - C_{10} -alkyl radical, such as methyl, ethyl and isopropyl radicals; preferably R^{13} is a C_1 - C_{10} alkyl radical;

each R^{14} , equal to or different from each other, is a hydrogen atom or a linear or branched, cyclic or acyclic, C_1 - C_{10} -alkyl radical; preferably R^{14} is a hydrogen atom or a C_1 - C_{10} alkyl radical;

R^{15} , equal to or different from each other, is a hydrogen atom or a linear or branched, cyclic or acyclic, C_1 - C_{20} -alkyl, C_2 - C_{20} alkenyl, C_2 - C_{20} alkynyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl or C_7 - C_{20} -arylalkyl radical optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; preferably R^{15} , equal to or different from each other, is a hydrogen atom or a linear or branched, cyclic or acyclic, C_1 - C_{20} -alkyl radical;

each R^{16} , equal to or different from each other, is a hydrogen atom or a C_1 - C_{15} -alkyl, C_2 - C_{15} alkenyl, C_2 - C_{15} alkynyl, C_6 - C_{15} -aryl, C_7 - C_{15} -alkylaryl or C_7 - C_{15} -arylalkyl radical; preferably R^{16} is a hydrogen atom.

Compounds belonging to formulas (II), (III), and (IV) are well known in the art. They are described for example in WO 96/23010, WO 97/02298, WO 98/40374, US 5,707,913 and *Organometallics* 2000, 19, 388.

The catalyst system object of the present invention can be used for (co)polymerizing one or more olefins. Therefore a further object of the present invention is a process for (co)polymerizing olefins containing from 2 to 20 carbon atoms comprising contacting one or more of said olefins under polymerization conditions in the presence of the catalyst system described above. Preferably alpha-olefins containing from 2 to 20 carbon atoms are used.

Examples of alpha-olefins that can be used with the process of the present invention are: ethylene, propylene, 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-octene, 4,6-dimethyl-1-heptene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene and 1-eicosene. Preferred olefins are propylene, ethylene 1-butene, 1-hexene and 1-octene.

The catalyst system object of the present invention are particularly suitable for the production of ethylene polymers having very high molecular weight. Thus a further object of the present invention is a process for polymerizing ethylene comprising contacting one or more of said olefins under polymerization conditions in the presence of the catalyst system described above.

Preferably the ethylene polymer obtainable with the catalyst system object of the present invention has a molecular weight Mw higher than 500,000; more preferably higher than 700,000; even more preferably higher than 1,000,000; still more preferably Mw can be higher than 1,300,000.

The following Examples are given for illustrative purpose and do not intend to limit the invention.

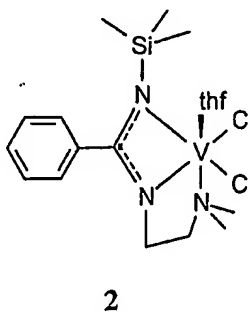
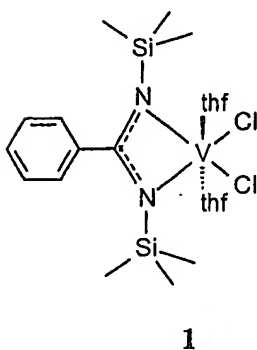
Materials and general procedures

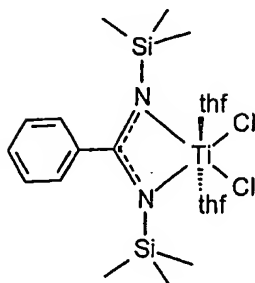
All manipulations were performed under an argon atmosphere using A glove box (Braun MB-150 GI or LM-130) and Schlenk techniques. Solvents were distilled from Na (toluene) or Na/benzophenone (heptane) and freeze-thaw degassed twice before use.

The vanadium aminidinate complexes **1** and **2** were prepared according to *Eur. J. Inorg. Chem.* 1998, 1867. The analogous titanium amidinate complexes **3** and **4** were prepared as follows:

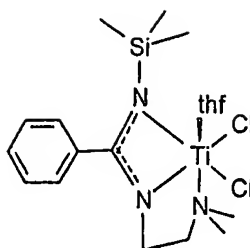
[{PhC(NSiMe₃)₂}TiCl₂(THF)₂] (**3**) was prepared by adding [PhC(NSiMe₃)₂]Li(THF) (1.1 g, 4.07 mmol) to a suspension of TiCl₃(THF)₃ (1.50 g, 4.05 mmol) in THF (*ca.* 100 mL) cooled to -78 °C. The mixture was allowed to warm to room temperature while stirring, affording a dark green-brown solution. After stirring overnight, the volatiles were removed *in vacuo* and the residue was "stripped" twice (2 x 10 mL) with petroleum ether (40-70 distillates). The residue was then extracted with hot toluene (*ca.* 40 mL) and cooled to -30 °C, yielding **3** as dark-green needles (0.77 g, 37 %).

[(Me₃SiNC(Ph)NCH₂CH₂NMe₂)TiCl₂(THF)] (**4**) was prepared by adding [(Me₃SiNC(Ph)NCH₂CH₂NMe₂)Li] (1.0 g, 3.69 mmol) to a suspension of TiCl₃(THF)₃ (1.37 g, 3.70 mmol) in THF (*ca.* 100 mL) cooled to -78 °C. Further steps were as described for (**3**), yielding **4** as brown-green needles (0.54, 32 %).



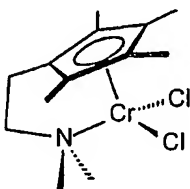


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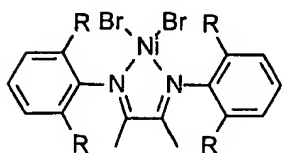
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The chromium complex 5 [$\eta^1:\eta^5$ -Me₂NCH₂CH₂C₅Me₄)CrCl₂] was prepared according to A. Döring, J. Göhre, P.W. Jolly, B. Kryger, J. Rust, G.P.J. Verhovnik, *Organometallics* **2000**, *19*, 388.

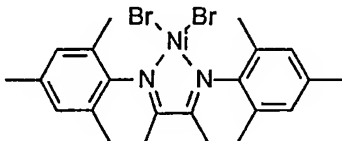


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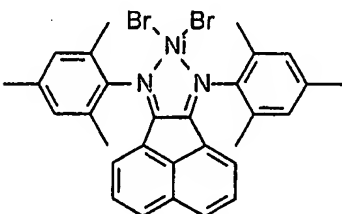
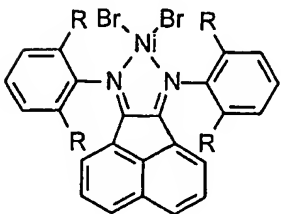
The nickel complexes 6 - 9 (R=isopropyl) were prepared according to procedures reported in: L.J. Johnson, C.M. Killian, M. Brookhart, *J. Amer. Chem. Soc.* **1995**, *117*, 6414, and R.J. Maldanis, J.S. Wood, A. Chandrasekaran, M.D. Rausch, J.C.W. Chien, *J. Organometal. Chem.* **2002**, *645*, 158.



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AlMe_3 (2M in hexane), AlEt_3 (25 wt.-% solution in toluene) and Al^nOct_3 (25 wt.-%, ca. 0.5M in hexanes) were obtained from Aldrich. Al^iBu_3 (1M solution in hexane) was purchased from Fluka.

Ethylene (3.5 grade supplied by Air Liquide) was purified by passing over columns of 4Å Molecular Sieves and BTS copper catalyst.

The Al and transition metal contents were determined by ICP / atomic absorption.

Surface area (BET) is determined according to BET methods (apparatus used: SORPTOMATIC 1800 from Carlo Erba).

The ethoxide content in the magnesium adducts was determined by GC analysis of the ethanol content of a solution obtained by dissolving 100 mg support in 5 mL *n*-BuOH containing a known quantity of *n*-PrOH as internal standard.

Preparation of partially dealcoholated adduct of formula $\text{MgCl}_2 \cdot w\text{UOH}$

The adduct $\text{MgCl}_2 \cdot 3\text{EtOH}$ was prepared according to the procedure described in Example 2 of US 4,399,054, operating at 3,000 rpm instead of at 10,000 rpm.

The adduct was partially dealcoholated by heating in a stream of nitrogen at temperatures increasing from 30°C. to 180°C.

Preparation of the support $\text{MgCl}_2/\text{AlQ}_j(\text{OEt})_{3-j}$

10-50 mL *n*-heptane were added to 1-5 g of a spherical adduct of magnesium chloride and ethanol under argon and the mixture was cooled to 0 °C. A 25-28 wt.-% solution of AlR_3 was then added gradually, over 5-10 min., to give a mol ratio $\text{AlR}_3/\text{EtOH} = 2$, the reaction being carried out in a standard Schlenk vessel equipped with a pressure release valve. The mixture was allowed to warm slowly to room temperature and the reaction was continued with occasional agitation for a further 1 day (AlMe_3), 2 days (AlEt_3), 3 days (Al^iBu_3) or 4 days (Al^nOct_3). The solid support was isolated by filtration, washed with heptane and petroleum ether (40-70) and then dried under a flow of argon and subsequently in vacuum. The compounds so obtained are reported in Table 1.

Preparation of the catalyst system - general procedure

A solution containing 1 µmol of the relevant transition metal complex (reported in Table 2) in toluene (1 mL) was added to 100 mg of support prepared as described above. The mixture was heated to 50 °C and kept at this temperature for 4 h. The toluene was then removed by decantation and the solid was reslurried in petroleum ether.

Polymerization - general procedure

Ethylene polymerization was carried out in a 1 L Premex autoclave equipped with a vortex stirrer. Petroleum ether (40-70, 450 mL) was introduced via a cannula. The reactor contents were stirred and heated to 50 °C. Triisobutylaluminium (TIBAL, 1 mmol) in petroleum ether (40-70, 10 mL) was introduced via the catalyst injection system. An ethylene overpressure of 0.5 MPa was applied and stirring continued for 5-10 min. A slurry of the immobilized catalyst (100 mg) in petroleum ether (40-70, 10 mL) was introduced through the catalyst injection system, which was then flushed with a further 50 mL petroleum ether (40-70). The ethylene pressure was increased to 1 MPa and kept constant for 2 h at a polymerization temperature of 50 °C, the stirrer speed being ca. 1000 rpm. After venting the reactor, the polymer slurry was mixed with 20 mL of acidified methanol, 50 mL demineralised water and 10 mL HCl (10 %). The polymer was recovered by filtration, washed with water (3 x 200 mL) and ethanol (2 x 30 mL) and dried in vacuo overnight at 70 °C. The polymerization results are reported in Table 2.

Table 1. Composition of $\text{MgCl}_2/\text{AlR}_n(\text{OEt})_{3-n}$ supports

Reactants		Product		Overall Composition
Starting material	Al alkyl	Al, wt.-%	OEt, wt.-%	
$\text{MgCl}_2 \cdot 1.1 \text{ EtOH}$	AlMe_3	5.16	6.2	$\text{MgCl}_2 \cdot 0.22 \text{ AlMe}_{2.28}(\text{OEt})_{0.72}$
$\text{MgCl}_2 \cdot 1.1 \text{ EtOH}$	AlEt_3	3.33	4.6	$\text{MgCl}_2 \cdot 0.14 \text{ AlEt}_{2.17}(\text{OEt})_{0.83}$
$\text{MgCl}_2 \cdot 1.1 \text{ EtOH}$	Al^iBu_3	3.00	3.3	$\text{MgCl}_2 \cdot 0.13 \text{ Al}^i\text{Bu}_{2.33}(\text{OEt})_{0.67}$
$\text{MgCl}_2 \cdot 1.1 \text{ EtOH}$	Al^nOct_3	1.96	0.9	$\text{MgCl}_2 \cdot 0.09 \text{ Al}^n\text{Oct}_{2.72}(\text{OEt})_{0.28}$
$\text{MgCl}_2 \cdot 2.1 \text{ EtOH}$	AlMe_3	8.06	9.4	$\text{MgCl}_2 \cdot 0.39 \text{ AlMe}_{2.30}(\text{OEt})_{0.70}$
$\text{MgCl}_2 \cdot 2.1 \text{ EtOH}$	AlEt_3	5.21	6.1	$\text{MgCl}_2 \cdot 0.24 \text{ AlEt}_{2.30}(\text{OEt})_{0.70}$
$\text{MgCl}_2 \cdot 2.1 \text{ EtOH}$	Al^iBu_3	3.32	3.9	$\text{MgCl}_2 \cdot 0.15 \text{ Al}^i\text{Bu}_{2.30}(\text{OEt})_{0.70}$
$\text{MgCl}_2 \cdot 2.1 \text{ EtOH}$	Al^nOct_3	2.61	1.3	$\text{MgCl}_2 \cdot 0.13 \text{ Al}^n\text{Oct}_{2.70}(\text{OEt})_{0.30}$

Table 2

run	complex	magnesium adduct	activity kg/mol. bar.h	Mw	Mw/Mn
1	1	$\text{MgCl}_2 \cdot 0.24\text{AlEt}_{2.30}(\text{OEt})_{0.70}$	3120	762,000.	2.0
2	2	$\text{MgCl}_2 \cdot 0.24\text{AlEt}_{2.30}(\text{OEt})_{0.70}$	1490	747,000	2.0
3	3	$\text{MgCl}_2 \cdot 0.24\text{AlEt}_{2.30}(\text{OEt})_{0.70}$	2250	602,000	2.3
4	4	$\text{MgCl}_2 \cdot 0.24\text{AlEt}_{2.30}(\text{OEt})_{0.70}$	1920	611,000	2.3
5	5	$\text{MgCl}_2 \cdot 0.22\text{AlMe}_{2.28}(\text{OEt})_{0.72}$	1910	1,396,000	1.8
6	5	$\text{MgCl}_2 \cdot 0.14\text{AlEt}_{2.17}(\text{OEt})_{0.83}$	2690	1,560,000	1.9
7	5	$\text{MgCl}_2 \cdot 0.13\text{Al}^i\text{Bu}_{2.33}(\text{OEt})_{0.67}$	1970	1,318,000	1.8
8	5	$\text{MgCl}_2 \cdot 0.09\text{Al}^n\text{Oct}_{2.72}(\text{OEt})_{0.28}$	1880	1,451,000	1.8
9	5	$\text{MgCl}_2 \cdot 0.39\text{AlMe}_{2.30}(\text{OEt})_{0.70}$	1780	n.a.	n.a.
10	5	$\text{MgCl}_2 \cdot 0.24\text{AlEt}_{2.30}(\text{OEt})_{0.70}$	2530	n.a.	n.a.
11	5	$\text{MgCl}_2 \cdot 0.15\text{Al}^i\text{Bu}_{2.30}(\text{OEt})_{0.70}$	1960	n.a.	n.a.
12	5	$\text{MgCl}_2 \cdot 0.13\text{Al}^n\text{Oct}_{2.70}(\text{OEt})_{0.30}$	1170	n.a.	n.a.
13	6	$\text{MgCl}_2 \cdot 0.24\text{AlEt}_{2.30}(\text{OEt})_{0.70}$	1190	1,300,000	2.3
14	6	$\text{MgCl}_2 \cdot 0.24\text{AlEt}_{2.30}(\text{OEt})_{0.70}$	1162	n.a.	n.a.
15	7	$\text{MgCl}_2 \cdot 0.24\text{AlEt}_{2.30}(\text{OEt})_{0.70}$	4224	300,000.	2.7
16	8	$\text{MgCl}_2 \cdot 0.24\text{AlEt}_{2.30}(\text{OEt})_{0.70}$	1242	n.a	n.a.
17	8	$\text{MgCl}_2 \cdot 0.24\text{AlEt}_{2.30}(\text{OEt})_{0.70}$	1270	510,000	2.1
18	9	$\text{MgCl}_2 \cdot 0.24\text{AlEt}_{2.30}(\text{OEt})_{0.70}$	7158	290,000	2.9
19*	9	$\text{MgCl}_2 \cdot 0.24\text{AlEt}_{2.30}(\text{OEt})_{0.70}$	11416	n.a.	n.a.

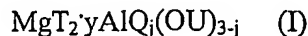
*=(30 min. polymerization)

n.a.= not available

Claims

1. A supported catalyst system comprising the product obtainable by contacting:

a) an adduct of formula (I)



wherein

Mg is magnesium; Al is aluminum; O is oxygen;

T is chlorine, bromine, or iodine;

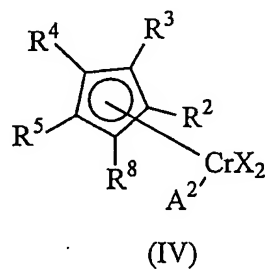
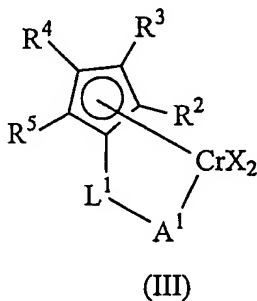
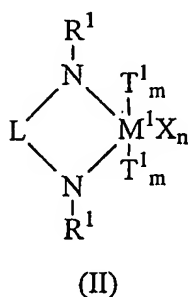
U is a linear or branched C₁-C₁₀ alkyl radical,

y ranges from 6.00 to 0.05;

j ranges from 3 to 0.1, being also a non integer number;

Q substituent, same or different, is a hydrocarbon radical containing from 1 to 20 carbon atoms optionally containing silicon or germanium atoms;

b) with at least one compound selected from the compounds of formula (II), (III) and (IV)



wherein

in the compound of formula (II)

M¹ is a transition metal atom selected from Groups 3-11 of Periodical Table (Group 3 including lanthanoids);

the substituents X, equal to or different from each other, are monoanionic sigma ligands selected from the group consisting of hydrogen, halogen, R, OR, OCOR, SR, NR₂ and PR₂, wherein R is a hydrocarbon radical containing from 1 to 20 carbon atoms optionally containing one or more Si or Ge atoms;

n ranges from 0 to 3;

the bonds connecting the two nitrogen atoms with the bridge L can be single bonds or double bonds;

each R^1 , equal to or different from each other, is a C_1 - C_{40} hydrocarbon radical optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements;

L is a divalent or trivalent bridge connecting the two nitrogen atoms;

m ranges from 0 to 1; when m is 0 the group T^1 is not-existent;

T^1 is a Lewis base; the group T^1 can also be bonded to the group R^1 ;

in the compound of formula (III):

Cr is a chromium atom; X is as described above;

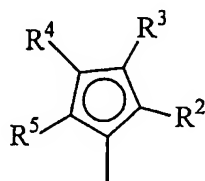
Each R^2 , R^3 , R^4 and R^5 , equal to or different from each other, is a hydrogen atom, a halogen atom, or a C_1 - C_{40} hydrocarbon radical optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; or two adjacent R^2 , R^3 , R^4 and R^5 form one or more C_3 - C_7 membered ring optional containing heteroatoms belonging to groups 13-17 of the periodic table;

L^1 is a divalent or trivalent bridging group selected from C_1 - C_{20} alkylidene, C_3 - C_{20} cycloalkylidene, C_6 - C_{20} arylidene, C_7 - C_{20} alkylarylidene, or C_7 - C_{20} arylalkylidene radicals optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements, and silylidene radical containing up to 5 silicon atoms such as $SiMe_2$, $SiPh_2$;

m_1 is 1 or 2, and more specifically m_1 is 1 when Z is N or P, and m_1 is 2 when Z is C, Si or Ge;

n_1 is an integer ranging from 1 to 4;

A^1 is a moiety of formula (V)



(V)

wherein R^2 , R^3 , R^4 and R^5 are as described above; or A^1 is an oxygen atom, a sulphur atom, a NR^7 , NR^7_2 , a OR^7 or a SR^7 group, wherein R^7 , is a C_1 - C_{40} hydrocarbon radical;

in the compound of formula (IV):

Cr is chromium; X, R^2 , R^3 , R^4 and R^5 are as described above, and R^8 has the same meaning given for R^2 , R^3 , R^4 and R^5 ;

A^2 is a halogen atom, R^7 , OR^7 , $OCOR^7$, SR^7 , NR^7_2 , NR^7_3 , SR^7_2 , OR^7_2 wherein R^7 are as described above.

2. The catalyst system according to claim 1 wherein T is chlorine; U is a linear C_1 - C_{10} alkyl radical; y ranges from 2 to 0.1; j ranges from 3 to 0.5 and Q is a linear or branched, cyclic or acyclic, C_1 - C_{20} -alkyl, C_2 - C_{20} alkenyl, C_2 - C_{20} alkynyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl or C_7 - C_{20} -arylalkyl radical optionally containing silicon or germanium atoms.
3. The catalyst system according to claims 1 or 2 wherein in the compound of formula (II) M^1 is a transition metal atom selected from Groups 3-6 and 8-10, X is a halogen atom or a R group; and L is a divalent or trivalent C_1 - C_{40} hydrocarbon group optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements.
4. The catalyst system according to any one of claims 1 to 3 wherein in the compound of formula (III) L^1 is a divalent group $(ZR^6_{m1})_{n1}$; Z being C, Si, Ge, N or P, and each R^6 group, equal to or different from each other, is a hydrogen atom or a hydrocarbon group containing from 1 to 20 carbon atoms, or two R^6 can form a aliphatic or aromatic C_4 - C_7 ring; R^7 is a C_1 - C_{20} -alkyl radical; and A^1 is a NR^7_2 group.
5. The catalyst system according to any one of claims 1 to 4 wherein the adduct of formula (I)

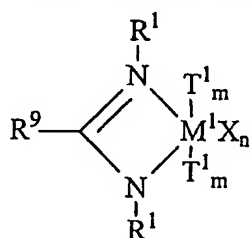


has a surface area (BET) higher than $30 \text{ m}^2/\text{g}$.

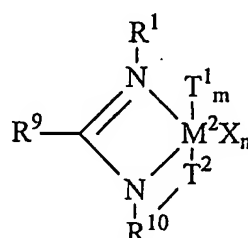
6. The catalyst system according to any one of claims 1 to 5 obtainable by the process comprising the following steps:
 - a) contacting
 - (i) a partially dealcoholated adduct of formula MgT_2wUOH wherein T is chlorine, bromine, or iodine; U is a linear or branched C_1 - C_{10} alkyl radical, w ranges from 6 to 0.1; with
 - (ii) an organo-aluminium compound of formula $H_eAlQ^1_{3-e}$ or $H_eAl_2Q^1_{6-e}$, wherein each Q^1 substituent, same or different, is a hydrogen atom, a halogen atom, or a hydrocarbon radical containing from 1 to 20 carbon atoms optionally containing silicon or germanium atoms; with the proviso that at least one Q^1 is different from halogen, and e ranges from 0 to 1, being also a non-integer number;

to obtain an adduct of formula (I) $\text{MgT}_2\text{yAlQ}_j(\text{OU})_{3-j}$ (I) described above;
and

- b) contacting the product obtained from step a) with at least one compound selected from the compounds of formula (II), (III) and (IV) as described in claim 1.
7. The catalyst system according to anyone of claims 1 to 6 wherein the amount of the compounds of formula (II), (III) or (IV) supported on the adduct of formula (I) is generally between 1000 $\mu\text{mol/g}$ of support and 1 $\mu\text{mol/g}$ of support.
8. The catalyst system according to anyone of claims 1 to 7 wherein the compound of formula (II) has formulas (IIa) or (IIb):



(IIa)



(IIb)

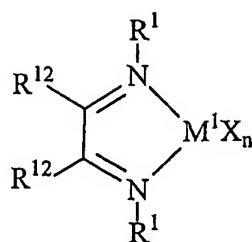
wherein R^1 , T^1 , M^1 , X , m and n are as described in claim 1;

R^9 is a hydrogen atom or a linear or branched, cyclic or acyclic, $\text{C}_1\text{-C}_{20}$ -alkyl, $\text{C}_2\text{-C}_{20}$ alkenyl, $\text{C}_2\text{-C}_{20}$ alkynyl, $\text{C}_6\text{-C}_{20}$ -aryl, $\text{C}_7\text{-C}_{20}$ -alkylaryl or $\text{C}_7\text{-C}_{20}$ -arylalkyl radical optionally containing heteroatoms belonging to groups 13-17 of the periodic table;

R^{10} is a divalent group selected from $\text{C}_1\text{-C}_{20}$ alkylidene, $\text{C}_3\text{-C}_{20}$ cycloalkylidene, $\text{C}_6\text{-C}_{20}$ arylidene, $\text{C}_7\text{-C}_{20}$ alkylarylidene, or $\text{C}_7\text{-C}_{20}$ arylalkylidene radicals optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements, and silylidene radical containing up to 5 silicon atoms;

T^2 is an OR^{11} , SR^{11} or a NR^{11}_2 radical, wherein R^{11} is a linear or branched, cyclic or acyclic, $\text{C}_1\text{-C}_{10}$ -alkyl, $\text{C}_2\text{-C}_{10}$ alkenyl, $\text{C}_2\text{-C}_{10}$ alkynyl, $\text{C}_6\text{-C}_{10}$ -aryl, $\text{C}_7\text{-C}_{10}$ -alkylaryl or $\text{C}_7\text{-C}_{10}$ -arylalkyl radical.

9. The catalyst system according to claim 8 wherein in the compounds of formula (IIa) and (IIb) T^1 is tetrahydrofuran or a tertiary amine; M^1 is titanium or vanadium; n is 2 and m is 1.
10. The catalyst system according to anyone of claims 1 to 7 wherein the compound of formula (II) has formula (IIc):

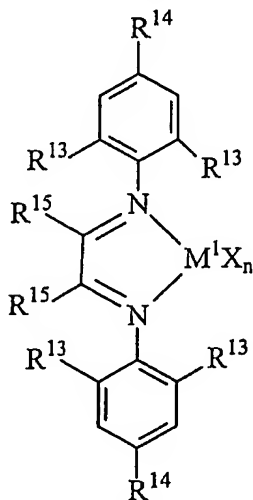


(IIc)

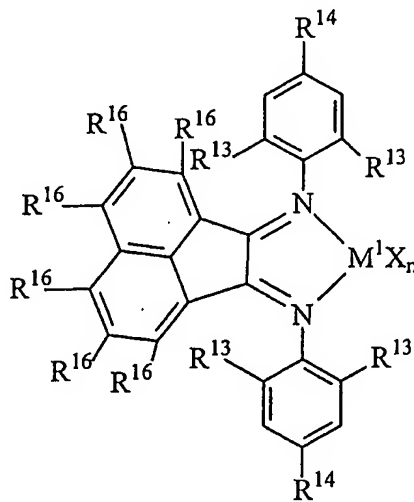
wherein R^1 , T^1 , M^1 , X , and n are as described in claim 1;

each R^{12} , equal to or different from each other, is a hydrogen atom or a linear or branched, cyclic or acyclic, C_1 - C_{20} -alkyl, C_2 - C_{20} alkenyl, C_2 - C_{20} alkynyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl or C_7 - C_{20} -arylalkyl radical optionally containing heteroatoms belonging to groups 13-17 of the periodic table; two R^{12} groups can also join to form a C_3 - C_8 membered ring that can bear one or more C_1 - C_{15} -alkyl, C_2 - C_{15} alkenyl, C_2 - C_{15} alkynyl, C_6 - C_{15} -aryl, C_7 - C_{15} -alkylaryl or C_7 - C_{15} -arylalkyl substituents.

11. The catalyst system according to claim 10 wherein the compound of formula (IIc) has formulas (IIca) or (IIcb):



(IIIca)



(IIIcb)

wherein:

each R^{13} , equal to or different from each other, is a hydrogen atom or a linear or branched, cyclic or acyclic, C_1 - C_{10} -alkyl radical;

each R^{14} , equal to or different from each other, is a hydrogen atom or a linear or branched, cyclic or acyclic, C_1 - C_{10} -alkyl radical;

- each R¹⁵, equal to or different from each other, is a hydrogen atom or a linear or branched, cyclic or acyclic, C₁-C₂₀-alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl or C₇-C₂₀-arylalkyl radical optionally containing heteroatoms belonging to groups 13-17 of the periodic table;
- each R¹⁶, equal to or different from each other, is a hydrogen atom or a C₁-C₁₅-alkyl, C₂-C₁₅ alkenyl, C₂-C₁₅ alkynyl, C₆-C₁₅-aryl, C₇-C₁₅-alkylaryl or C₇-C₁₅-arylalkyl radical.
12. A process for (co)polymerizing olefins containing from 2 to 20 carbon atoms comprising contacting one or more of said olefins under polymerization conditions in the presence of the catalyst system of claims 1-11.
13. The process according to claim 12 wherein one or more alpha-olefins are (co)polymerized.
14. The process according to claim 12 wherein said alpha olefins are propylene, ethylene, 1-butene, 1-hexene and 1-octene.
15. A process for polymerizing ethylene comprising contacting one or more of said olefins under polymerization conditions in the presence of the catalyst system of claims 1-11.
16. The process according to claim 15 wherein the ethylene polymer has a molecular weight Mw higher than 500,000.